# Synthesis and Chemical Modification of New Epoxy Resins Containing Alkylaminopyridines

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**ABSTRACT:** A new series of epoxy resins containing 4-(*N,N*-dialkylamine)pyridines (DAAP) functionality was prepared by reaction of 4-aminopyridine or/and aniline with epichlorohydrin. Then, hydroxyl groups in the polymeric chain underwent a chemical modification with acyl chloride. Modification of the side group and backbone of the chain resulted in an enhancement of solubility of the linear catalyst with catalyzed system and also led to an accelerated acylation. Here, acetylation of *tert*-butyl alcohol was monitored by means of chromatographic analyses for determining the catalytic power of these polymeric catalysts. Catalytic activity of the modified linear poly(4-aminopyridine-epichlorohydrin-aniline) was found to be more effective than that of DMAP, and catalytic activity of network polymers in a heterogeneous system was found to be somewhat lower than that of any of its linear analogs. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1101–1105, 1999

**Key words:** alkylaminopyridines; supernucleophilic reagent; epoxy polymer; acylation

## INTRODUCTION

It is well known that 4-(*N,N*-dimethylamino)pyridines (DMAP) are costly, although highly efficient, acylation catalysts. To produce a commercial polymeric catalyst, high catalytic activity, cheap and capable of being used repeatedly, is one of the goals pursued by researchers in this field.

To our knowledge, only two processes of obtaining such polymeric catalysts have been put forward so far. One developed a polymer-supported dialkylaminopyridine catalyst. Shinkai et al. have covalently linked DMAP to crosslinked polystyrene (PS),[1] and Klotz et al. dealt with reaction of several carboxylic acid containing aminopyridines with commercial poly(ethylenimine) (PEI).[2] The other exploited a synthesis of poly(aminopyridine)s. Klotz et al. claimed that the aminopyridines that they have prepared includes the dipro-

pionate, which could be condensed with a diamine to obtain a polyamide with supernucleophiles.[3] Mathias et al. successfully prepared 4-(*N,N*-diallylamino)pyridine (DAAP) and then obtained a homopolymer and copolymers of DAAP.[4] Zeldin et al. produced silanes and siloxanes incorporating DAAP functionality.[5] Sun et al.[6] tentatively synthesized a polyurethane with supernucleophilic reagents.

Apart from containing catalytic groups with desirable density, an excellent commercial polymeric catalyst must also demonstrate proper accessibility in relation to its substrates in the form of good solubility shown by their linear analogs in a catalyzed system and of highly efficient catalytic activity. Moreover, the macromolecular network formed of such a polymeric catalyst should not only give little of steric hindrance to reactants and products, but also have favorable mechanical properties.

We became interested in the preparation and chemical modification of new epoxy resins containing supernucleophilic functions that could

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**Scheme 1**

lead to obtain high-efficient polymeric catalysts for acylation. We synthesized epoxy resin **1** by a one-step reaction of 4-aminopyridine with epichlorohydrin following the process reported in a previous paper.[7] Then, we permuted hydroxyl groups of **1** into esters to obtain epoxy resin **2.** On the other hand, we synthesized epoxy resin **3** by reaction of 4-aminopyridine and aniline with epichlorohydrin, and then modified it using acyl chlorides to give epoxy resin **4.**

To produce catalysts capable of repeated uses, linear epoxy chains must be crosslinked with some crosslinking agents to form network polymeric products. Linear polymer **3** can be netted involving *p*-phthaloyl dichloride or tolyene-2,4-diisocyanate to yield either of the two crosslinked polymers, **5a** and **5b,** which can be modified into **6a** and **6b.**

A preliminary test of the catalysts thus yielded was carried out in a simple acetylation of *tert*-butyl alcohol in presence of epoxy resins **1, 2, 4, 6a, 6b,** or DMAP. Results from the test showed that, compared to the rate of an uncatalyzed reaction, the rate of a catalyzed reaction using any of the modified epoxy resins just specified was decidedly faster, whereas the rate of reaction using epoxy resin **4** was significantly faster than that of a catalyzed reaction using DMAP.

## RESULTS  AND  DISCUSSION

Any of the epoxy resins that contain 4-dialkylaminopyridines is a polymeric catalyst that can be prepared conveniently in a mild reaction condition, a rapid one-step reaction of 4-aminopyridine with epichlorohydrin. The macromolecular chains thus obtained are structurally stable and hydrophilic. Like reactive polymer, a large number of hydroxyl groups in the chains, as side groups, may be involved in reaction with acyl chlorides or isocyanates so as to be modified or crosslinked into corresponding polymeric catalysts to be used for acylation (Scheme 1).

However, crude linear epoxy resin can be dissolved in water instead of in organic solvents, because macromolecules are linked to a great number of strongly hydrophilic groups (such as hydroxyl group and aminopyridine). Insolubility of the linear polymers entails decreased accessibility between the catalytic site and the substrate (such as acid anhydride or acyl chloride) in the catalyzed system because of folding and snarling of the macromolecular coils. On the other hand, tending to undergo acylation, the hydroxyl groups in the chains (secondary alcohol) as a competitive inhibitor on the polymer would exert suppression over acylation of other high-steric hindrance alcohol or amines. These two effects would abate the catalytic capacity in such epoxy resins and impel them to carry out a chemical modification.

Two chemical modification methods were designed. One method was aimed at achieving "chemical modification of the side group," which calls for capping by a protective group of the hydroxyl groups on chain. Some reagents, to be used as protective groups, are used tentatively for occluding the hydroxyl groups; for example, etherification of the hydroxyl groups by dimethyl sulfonate and esterification of the hydroxyl groups by various acyl chlorides (e.g., benzoyl chloride, phenyl acetic chloride, cinnamic chloride, acetyl chloride, and *n*-octadecanoyl chloride). As the experimental results indicated, either dimethyl sulfonate or various aliphatic acyl chlorides on the chains could be effectively eliminated by the hydroxyl groups, yet the solubility of such resin was not increased. But the esterification pluging using aromatic acyl chlorides, [i.e., esterification of the hydroxyl groups with benzoyl chloride (Scheme 2), phenyl acetic chloride, or cinnamic chloride] led to not only an conversion of the alcohol into esters but also decreased solubility parameters of the polymeric catalysts so as to markedly improve the solubility and catalytic activity of the linear polymers in the acetylation of *tert*-butyl alcohol.

The other method designed is a chemical modification of backbone. To meliorate hydrophobility



**Scheme 2**

**Scheme 3**

of the chains, aniline, as a third component, was mixed into a step-polymerization of 4-aminopyridine with epichlorohydrin (Scheme 3). Thus a great number of hydrophobic phenyl rings were made to hang onto the hydrophilic backbone of catalyst, and then the hydroxyl groups were modified by benzoyl chloride (Scheme 4). By applying this approach, the ratio of the hydrophobic aniline units to hydrophilic aminopyridine units could be adjusted to effect a change in the solubility parameter of the polymeric catalyst such that the solubility parameter would become similar in value to that of the catalyzed system. This would enable the linear polymeric catalyst to dissolve in any acylation system.

Moreover, in most cases, a tertiary amine (such as triethylamine) must be appended to the acylation as an assistant catalyst when any of the other alkylaminopyridines (such as DMAP) is used. This is necessary to bring about a simultaneous presence of both the main catalyst and the cocatalyst in a polymeric chain, because the presence of a number of aniline units in the chain has the same effect as is caused by the presence of unit of a tertiary amines in chain.

To manufacture a catalyst that is capable of being used repeatedly, a certain crosslinking agent was adopted for forming a retiform struc-



**Scheme 4**



**Scheme 5**

ture from a linear polymer. Because an epoxy chain contains a large number of hydroxyl groups, both **1** and **3,** unmodified epoxy resins, were crosslinked with an appropriate amount of di(acyl chloride) or diisocyanate. Then the residuary hydroxyl groups in network polymer were further modified by benzoyl chloride into a polymeric catalyst once again available (Scheme 5). The crosslinked polymeric catalysts that merely swell but do not dissolve in acylation system could be separated from catalyzed system by simple filtration, and thus used repeatedly.

The crosslinking density of the crosslinking polymer can significantly affect its quality and catalytic power. Within the limit of hydroxyl groups, the greater quality of crosslinking agent used, the lower the degree of swelling and the less the mesh of the crosslinking structure; moreover, the diffusion rate of reactants and products in network of the polymeric catalyst remained low. However, if the crosslinking agent was used in a small quantity, then the mechanical properties of the catalyst stayed poor.

Acetylation of *tert*-butyl alcohol was monitored by gas chromatography (Fig. 1). The content of *tert*-butyl alcohol in the solution was measured at regular intervals and compared to the internal standard compound for calculating the conversion for *tert*-butyl alcohol. The findings are as follows.

**Figure 1**  Acetylation of *tert*-butyl alcohol with acetic anhydride in presence of **4** (○), DMAP (+), **6a** (△), **6b** (▲), **2** (■), **1** and no catalyst (□).

1. Catalytic activity of epoxy resin **1** was low. This is believed to have been caused by the mutual inaccessibility between the molecules of the reactant and the catalytic groups.
2. Catalytic activities of the network polymeric catalysts **6a** and **6b** were lower than that of their corresponding linear analogs. This is considered to have arisen from both the steric hindrance of substrates interpenetrating toward the inside of the macromolecular net and the jam of product evacuating toward the outside of the net.
3. No sign of weakened catalytic power was detected in any of such crosslinked polymers after it had been used consecutively for five times in the acetylation. This indicates that the macromolecular chain was stable and that the linking between the polymeric carrier and the active group was firm. Mensurations based differential scanning calorimetry (DSC) and TG analyses set the heat decomposition temperature of **6a** at around 390°C.
4. The linear polymeric catalysts became excellent catalysts for acylation after their side groups and backbone sequence had undergone chemical modification. The catalytic activity of epoxy resin **4** is higher than that of DMAP.

## EXPERIMENTAL

Infrared spectra were measured on a Nicolet 205 Fourier transform-infrared spectroscopy (FTIR). $^1$H-NMR spectra were recorded at 200 MHz on a Bruker AP-P200 spectrometer. Elemental analyses were run by a PE-2400. Acetylation reactions were followed by a GLC on Beifen SQ206 in the flame-ionization mode with a 2 m stainless steel column of GD $\times$ 101 10% poly(ethylene glycol) 20*M* at 170°C. Thermal analysis was performed under nitrogen on a Mettler DSC30 and TG50 system interfaced with a Mettler TA 3000 minicomputer.

### Preparation of Linear Poly(*p*-aminopyridine-epichlorohydrin) (1)

To a solution of 10.00 g (0.106 mol) of 4-aminopyridine in 20 mL of *N,N*-dimethylformide (DMF) was added 9.83 g (0.106 mol) of epichlorohydrin. The mixture was stirred for 3 h at room temperature and was evaporated under reduced pressure, with the residue dissolved in $H_2O$. Then the product was precipitated from acetone to give 12.9 g (81%) of **1** as a white jelly matter.

ANAL. Calcd for $C_8H_{10}N_2O$: C, 63.98%; H, 6.71%; N, 18.65%. Found: C, 64.02%; H, 6.73%; N, 18.59%. IR: 3400, 3140, 1650–1500, 1200 cm$^{-1}$. NMR ($D_2O$): 3.22(d, 2H); 4.45(m, 1H); 7.20(d, 2H); 8.32(d, 2H).

### Modification of Linear Poly(*p*-aminopyridine-epichlorohydrin) by Benzoyl Chloride (2)

To a mixture of 10.0 g of **1** (including 66.6 mmol of hydroxyl groups) in 20 mL of DMF under dry atmosphere at 0°C was added 15 g (0.1 mol) of benzoyl chloride slowly, and the solution was stirred for 2 h at room temperature. The mixture was washed three times with ether, evaporated under reduced pressure, and precipitated in acetone. The pale yellow solid was filtered and dried under vacuum to give 15.9 g (94%) of **2** as a pale yellow jelly matter.

ANAL. Calcd for $C_{15}H_{14}N_2O_2$: C, 70.85%; H, 5.56%; N, 11.02%. Found: C, 70.88%; H, 5.59%; N, 10.97%. IR: 3420, 1700, 1650–1500, 1124 cm$^{-1}$. NMR ($D_2O$): 3.03(d, 2H); 4.68(m, 1H); 7.90(d, 2H); 8.18(d, 2H); 8.46(d, 2H); 8.90(d, 2H).

### Preparation of Linear Poly(*p*-aminopyridine-epichlorohydrin-aniline) (3)

To a solution of 10.00 g (0.106 mol) of 4-aminopyridine, 9.89 g (0.106 mol) of aniline in 20 mL of

DMF was added. After the mixture was stirred for 5 min, 19.66 g (0.21 mol) of epichlorohydrin was added. The mixture was stirred for 3 h at room temperature and was evaporated under reduced pressure. The residue was dissolved in $H_2O$. Then the product was precipitated from acetone, filtered, and dried under vacuum to give 24.2 g (76%) of epoxy resin **3** as a yellowish jelly solid.

ANAL. Calcd for $C_{17}H_{21}N_3O_2$: C, 68.21%; H, 7.07%; N, 14.04%. Found: C, 68.23%; H, 7.10%; N, 13.99%. IR: 3400, 3140, 1650–1500 $cm^{-1}$. NMR ($D_2O$): 2.42(d, 2H); 4.60(m, 1H); 7.20(d, 2H); 7.48(d, 2H); 8.30(d, 2H).

### Modification of Linear Poly(*p*-aminopyridine-epichlorohydrin-aniline) by Benzoyl Chloride (4)

To a mixture of 20.0 g of epoxy resin **3** (including 0.13 mol of hydroxyl groups) in 40 mL of DMF under dry atmosphere at 0°C was added tardily 25 g (0.18 mol) of benzoyl chloride, and the solution was stirred for 2 h at room temperature. The mixture was washed three times with ether, evaporated under reduced pressure, and precipitated in acetone. The pale yellow solid was filtered and dried under vacuum to give 31.2 g (92%) of epoxy resin **4.**

ANAL. Calcd for $C_{31}H_{29}N_3O_4$: C, 73.35%; H, 5.76%; N, 8.28%. Found: C, 73.30%; H, 5.75%; N, 8.32%. IR: 3420, 1720, 1650–1500 $cm^{-1}$. NMR ($D_2O$): 2.62(d, 2H); 4.78(m, 1H); 7.98(d, 2H); 8.40(d, 2H); 8.62(d, 2H); 8.90(d, 2H).

### Crosslinking of Poly(*p*-aminopyridine-epichlorohydrin-aniline) by *p*-Phthaloyl Chloride (5a)

To a mixture of 20.0 g of **3** (including 0.13 mol of hydroxyl group) in 30 mL of DMF under dry atmosphere at 0°C was added 13.57 g (66.8 mmol) of *p*-phthaloyl dichloride, and the solution was stirred for 2 h at room temperature. The precipitate was filtered from the solution and washed for 10 h with $H_2O$ in a Soxhlet extractor. The white powder was dried under vacuum to give 19.6 g (63%) of **5a.**

### Crosslinking of Poly(*p*-aminopyridine-epichlorohydrin-aniline) by Toluene-2,4-Diisocyanale (5b)

To a mixture of 20.0 g of **3** (including 0.13 mol of hydroxyl group) in 30 mL of DMF under dry at-

mosphere at 0°C was added 11.64 g (66.8 mmol) of tolyene-2,4-diisocyanate, and the solution was stirred for 3 h at room temperature. The precipitate was filtered and washed for 10 h with $H_2O$ by a Soxhlet extractor. The white powder was dried at 25°C under vacuum to give 17.1 g (54%) of **5b.**

### Modification of Network Poly(*p*-aminopyridine-epichlorohydrin-aniline) by Benzoyl Chloride (6a, 6b)

To a solution of 6 g (42.7 mmol) of benzoyl chloride in 20 mL of DMF was added 10.0 g of **5a** (including 21.5 mmol of hydroxyl groups) [or 10.0 g of **5b** (including 22.1 mmol of hydroxyl groups)]. The mixture was stirred for 2 h at room temperature. The solid was filtered, washed with $H_2O$ by a Soxhlet extractor, and dried under vacuum to give 10.6 g (87%) of **6a** [or 10.5 g (85%) of **6b**] as a white powder.

### Evaluation of the Catalysts in Acetylation of *tert*-Butyl Alcohol

A mixture of 40.8 g (0.4 mol) of acetic anhydride, 15 mL of heptane (internal standard compound), and 10.1 mmol of polymeric catalyst (5 mol % of alcohol) was placed in a thermostatically cell at desired reaction temperature (25°C). After stirring under nitrogen for 15 min, 15.0 g (0.2 mol) of *tert*-butyl alcohol was added while stirring continued. The progress of the reaction was monitored by timely withdrawal of 0.02 $\mu$L aliquots for chromatographic analysis.

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